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H. D. Robinson

A Study of the Benzidine
Rearrangement



THE
UNIVERSITY
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**A STUDY OF THE BENZIDINE
REARRANGEMENT**

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... Bachelor of Science.....

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FOREWORD.

I wish to express to Dr. Oliver Kamm, under whom this work was undertaken, my deep appreciation of his many and valuable suggestions during the progress of the experiments.



A STUDY OF THE BENZIDINE REARRANGEMENT.

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INTRODUCTION.

The purpose of this work is to study the benzidine rearrangement by means of the conversion of O-hydrazoanisol into dianisidine. Both from the theoretical and practical standpoints it seemed of importance to study the rearrangement under varying conditions of temperature and concentrations of acid and to seek the best conditions suited for this conversion.

A secondary purpose is the study of the preparation of hydrazoanisol from the standpoint of improving the methods now available in the literature.

For this purpose I attempted to prepare hydrazoanisol by as cheap and efficient ^amethod as possible.

HISTORICAL PART.

All the references in the literature give the preparation of hydrazoanisol as analogous to the preparation of hydrazobenzene, and so it seems important to outline the history and theory of the preparation of hydrazobenzene and its rearrangement, and to use this information as a foundation for the subsequent laboratory work.

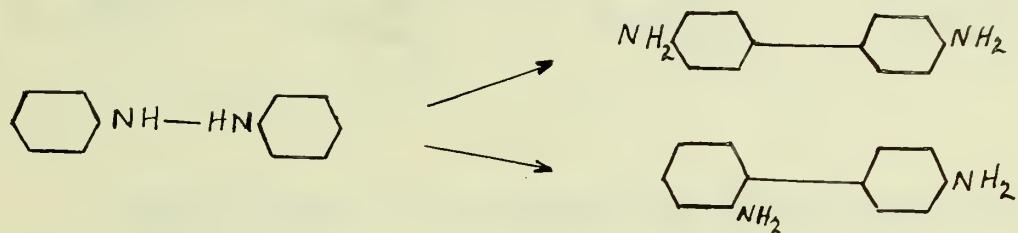
Zinin¹ and Gerhert² in 1845 first prepared benzidine in the form of its sulfate, when they found that when azobenzene is reduced and boiled with sulfuric acid, benzidine, or *pp'*-diaminodiphenyl is formed.

Von P. Alexeyeff³ demonstrated the intermediate product in this rearrangement to be hydrazobenzene. He also showed that hydrazobenzene could be prepared by reducing nitrobenzene with zinc and sodium hydroxide in an alcoholic solution.

Schultz⁴ prepared benzidine by treating azobenzene with alcoholic ammonia and passing in sulfur dioxide gas. By diluting the alcoholic solution, he separated hydrazobenzene. This compound when heated with hydrochloric acid was rearranged to benzidine. He believed it was not necessary to first form the hydrazo compound for when he treated azo benzene with an alcoholic solution of stannous chloride and hydrochloric acid, benzidine was also formed; in fact, ^{as} fast as the hydrazobenzene was formed it was rearranged to benzidine. He obtained about a forty-two per cent yield by this method.

A. W. Hofman⁵ also showed that the intermediate product, hydrazobenzene, was formed during the reduction and showed this to be the compound that is rearranged to benzidine.

Schultz⁶ took up the investigation and discovered a small quantity of a second isomer called diphenyline which is produced simultaneously with benzidine. The reactions are represented by the following equations:



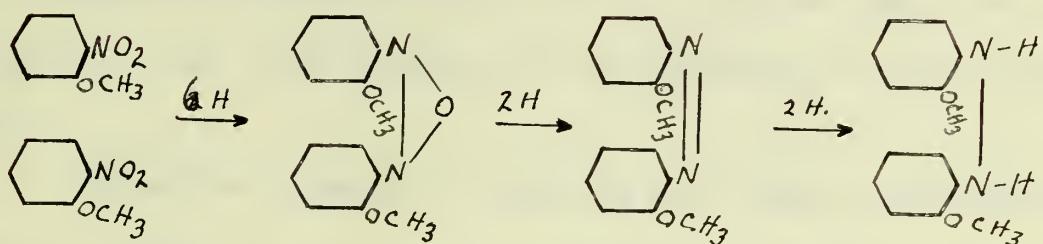
It was found later by Jacobson⁷ that heat favors the formation to diphenyline. Jacobson⁷ and his pupils studied other side reactions under varying conditions, and presented generalizations in regard to the rearrangement of substituted hydrozobenzenes.

Elbs⁸ and Schwartz⁸ in 1899 prepared hydrazobenzene by the electrolytic reduction of nitrobenzene and obtained a yield of about eighty per cent of the theoretical amount.

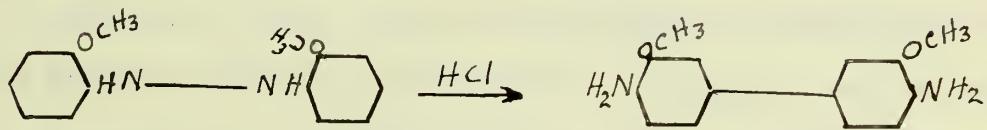
Schultz⁹ has given directions for the preparation of hydrazoanisol by the reduction O-nitro-anisol with zinc dust in an alcoholic solution of sodium hydroxide as well as for the rearrangement of the crude product to dianisidine.

THEORETICAL PART.

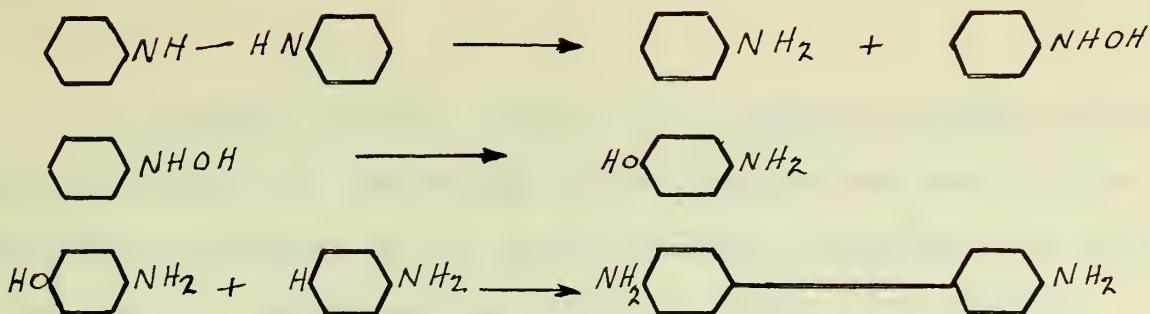
Hydrazoanisole is obtained by reducing O-nitroanisole with zinc dust in alkaline solution by the following steps:



Hydrazoanisole is rearranged to dianisidine in the following manner:

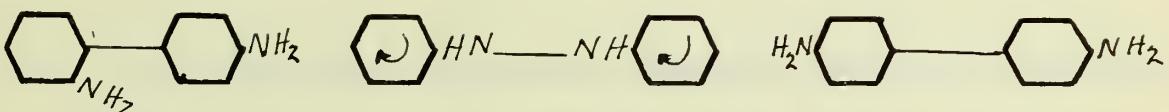


Many theories have been advanced to explain why hydrazo compounds are isomerized in the presence of acids. It was first thought that the catalytic action of the acid was the function of the hydrogen ion but since the rearrangement takes place in indifferent solvents and even with dry hydrochloric acid gas, this explanation was rejected. Then it was assumed that there is a hydrolysis of the nitrogen group to aniline and phenylhydroxylamine. This would rearrange to para amido phenol and condense with aniline in the para position.



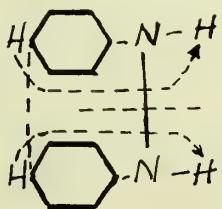
This attempted explanation does not fit with the facts for both components of the last equation do not condense to yield benzidine.

From the formulae it will be seen that the attachment

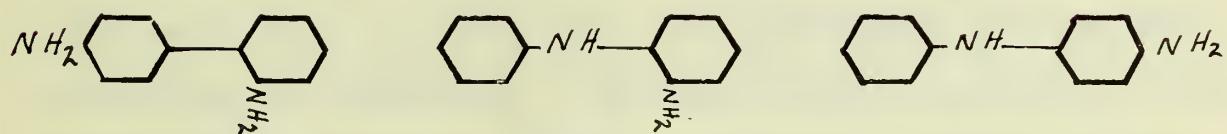


between the two nitrogen atoms in hydrazobenzene is substituted by that between two carbon atoms of the nuclei; the amino groups being transferred to the two para positions in benzidine or to one para and one ortho in diphenyline. A simple way of visualizing the change is to suppose the two nuclei in the hydrazobenzene to separate and in the first instance to make a complete revolution before joining up again or, in the other case, for one nuclei to be turned through 180° while the other turns through 60° .

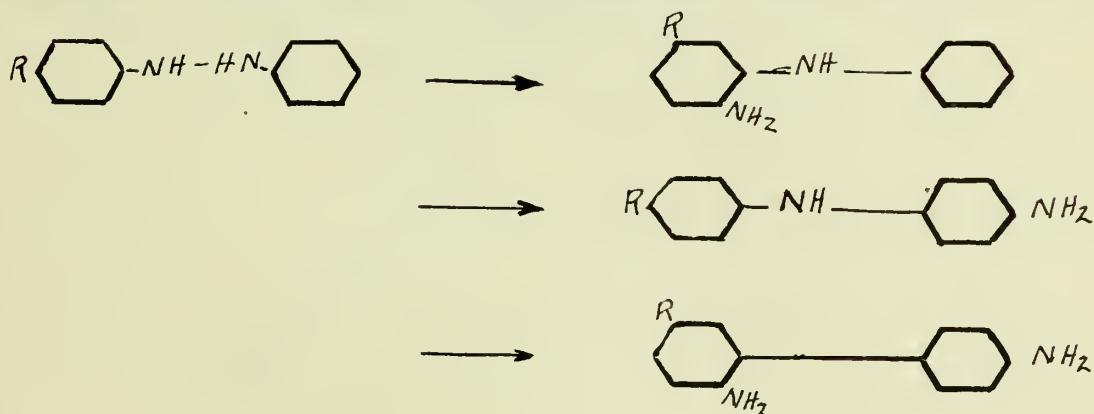
H. Wieland¹¹ states, "We have to consider the benzidine rearrangement as an intramolecular stabilization reaction in which the meta stable arrangement of the hydrazo system varies as the change of grouping."



Jacobson⁷ and his pupils, in a series of papers, have given the results of subjecting hydrazobenzene and some of its substituted compounds to the action of acid. They gave as some of the possible compounds that could be formed from hydrazobenzene, the following:



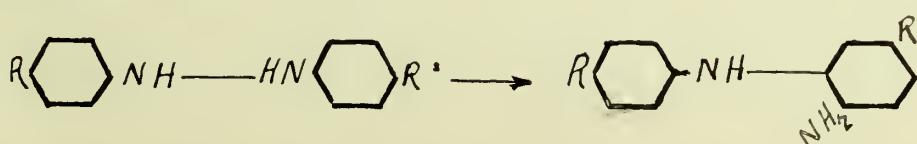
The following changes are possible supposing one nuclei to be substituted in the para position:



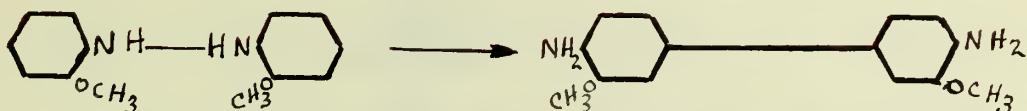
Decomposition of compound into two molecules of base, thus:



Also substitution of both para positions gives the following compounds:

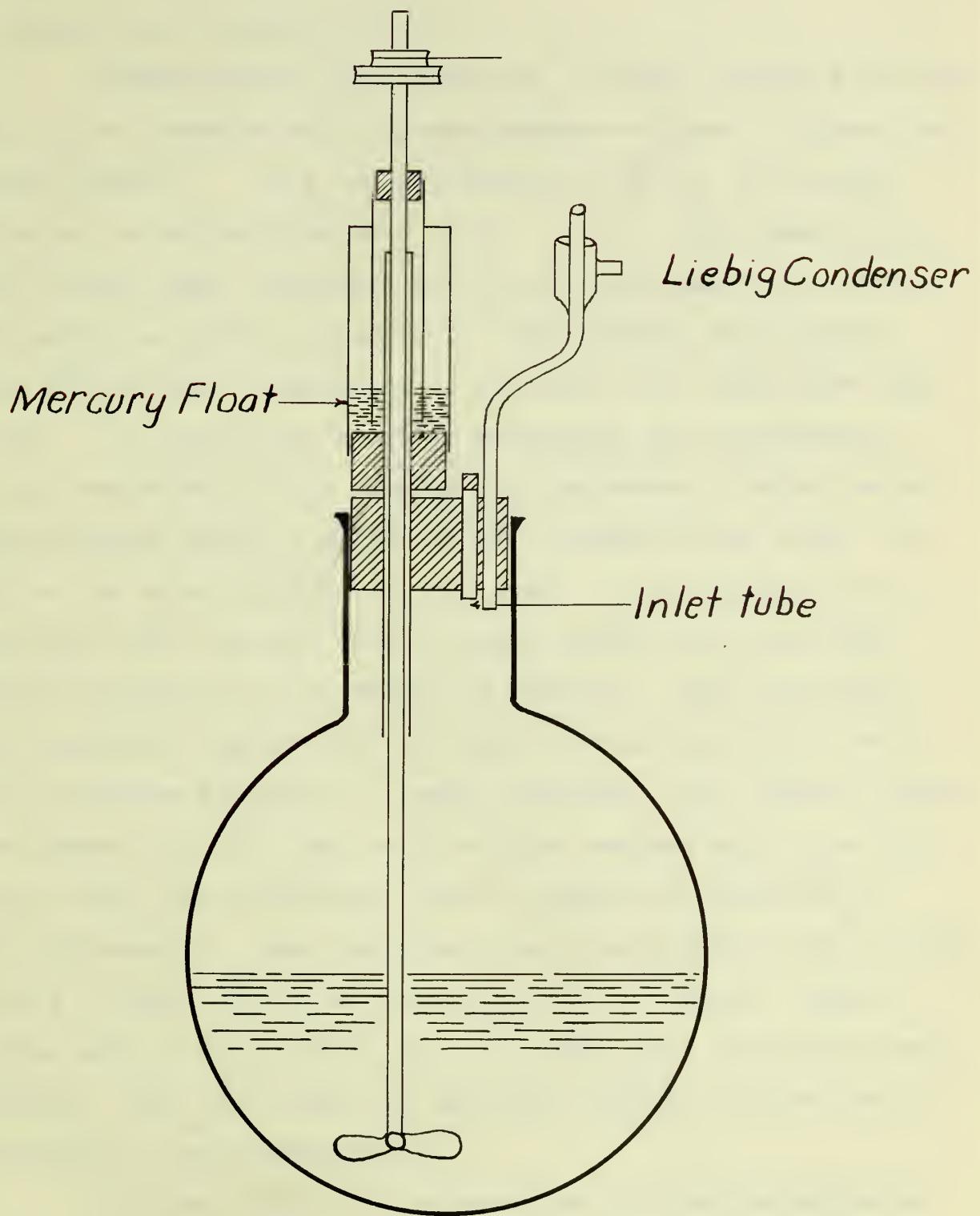


Also both ortho substituted, gives compounds as shown below:



It has been shown that all these reactions may and occasionally do occur, but usually the principal changes are limited to one, or at the most, two reactions; that the other reactions are subordinate. The main point of interest is that substituting both para positions generally determines decomposition into two molecules of base and that the presence of methyl groups in the ortho positions to the azo group, irrespective of the nuclei, diminishes the ortho semidine conversion.

DIAGRAM I



L. M. F. INC.

1000

10

1000000000

1000000000
1000000000
1000000000

1000000000



EXPERIMENTAL PART.

I. Preparation of Hydrazoanisol:

Hydrazoanisol was prepared by a method analogous to that used for the preparation of hydrazobenzene as given in Noyes' Laboratory Manual.¹⁰ 30 g. of nitrobenzene, 200 cc. of alcohol, and 40 cc. of sodium hydroxide (3 cc. - 1 g.) were placed in a round-bottom flask, connected with an air condenser and a mechanical stirrer as shown in Diagram I. This mixture was heated to about 75° and small quantities of zinc dust were added from time to time. As long as the solution maintained this temperature, no zinc was added; but as soon as the temperature lowered, more zinc was added until 45 g. in all were placed in the flask. As soon as the solution appeared colorless, it was filtered hot to remove the zinc and zinc oxide, cooled quickly, and the hydrazoanisol filtered off as rapidly as possible. The precipitate was transferred immediately to a flask containing alcohol and a little ammonium sulphide to prevent oxidation. The mother liquors were placed into the flask with the zinc residue and heated, filtered, cooled and refiltered again to obtain the remainder of the hydrazoanisol. The precipitate was recrystallized from alcohol. A yield of about 87% of the theoretical was obtained. Another run was made by this method, so that checks upon the results were obtained. This yield does not take into account the loss due to solubility of the hydrazoanisol.

The next series of preparations of hydrazoanisol were made to try and eliminate the large quantities of alcohol used.

So instead of 200 cc. of alcohol, only 25 cc. were used and 100 cc. of water. The procedure was the same up to the point where the solution became colorless showing that reduction was complete. At this point 500 cc. of water were added and the solution was shaken and filtered through a sieve (100 mesh). The hydrazoanisol was retained in the sieve and washed with very dilute hydrochloric acid. The precipitate was placed in a flask containing alcohol and ammonium sulfide and later recrystallized from alcohol. A yield of 85% of the theoretical was obtained.

The preparation of hydrazoanisol was attempted without the use of alcohol. No results were obtained for the O-nitro anisol remained unchanged.

It is therefore possible to eliminate most of the large quantity of alcohol used in Noyes' Laboratory Manual and obtain just as good yields by using a very dilute solution of alcohol. When a small quantity of alcohol is used the reduction mixture should not be allowed to exceed 60°-65° in temperature, for if the reduction is too fast and the temperature high, the yields obtained will not be so great. In order to keep the temperature down the zinc dust was added very slowly and the mechanical stirrer distributed it throughout the whole solution. Also, the precipitate does not have to be heated and filtered three or four times in order to remove the zinc. The precipitate of hydrazoanisol is handled much easier and with less time, thereby allowing it less chance to be oxidized by the air, so a pure product is obtained.

III. Rearrangement of Hydrazoanisol to ~~D~~inisidine.

Very little material was found in the literature about the rearrangement of hydrazoanisol. Noyes, Cohen, and Gatterman, in their laboratory manuals suggest the use of concentrated hydrochloric acid for the conversion of hydrazobenzene into benzidine, and Gatterman states that the rearrangement of hydrazoanisol is similar to that of hydrazobenzene. None mention the temperature and time for the best yields, so a series of conversions were run to obtain not only the best concentrations of acid but the conditions of temperature and time for the best yields.

Accordingly, 0.4 gram samples of hydrazoanisol were weighed and placed into small flasks and covered by 20 cc. portions of HCl of the following concentrations, 2 N HCl, 4 N HCl, N HCl and 0.5 N HCl, and concentrated acid, and shaken. In all cases a green precipitate was formed. The precipitate would not go into solution although the solution was diluted up to 100 cc. This precipitate was ~~d~~inisidine hydrochloride. In order to explain this, a 0.4 g. sample of pure ~~d~~inisidine was placed in a flask and 10 cc. of water added. Concentrated HCl was added drop by drop and the solution shaken vigorously. After a few drops of HCl were added, the precipitate went into solution showing that the hydrochloride was soluble in a very dilute acid, ^{but in more concentrated acid it} and required heat to place it into solution. A series of conversions were run to obtain the best yields in different acid concentrations and different temperatures varying from room temperature to 100°. 20 cc. portions of HCl acid were used of

the following concentrations, 2%, 3%, 5% 7.5%, 10%, 37% and with the temperature being maintained at 20°, 40°, 60°, and 100°, by constant heating and stirring on a hot plate. The portions were shaken for thirty minutes and filtered. The dinitroso was precipitated in the form of the chromate salt. The results show that the use of concentrated or 37% acid at 60° gave the best results, while good results were obtained at room temperature and 2% acid. The results of the conversions are best shown by the curves following:

Curve I gives the per cent yields of rearranged hydrazoanisol at 20° C. and with different concentrations of acid. When from 2% to 5% acid is used the conversion seems to work well at room temperature, but with more concentrated acid the per cent yields are not so great due to the formation of hydrochloride which is salted out and requires heat to place it into solution.

Curve II and III give the per cent yields at 40° and 60° with different concentrations of acids. The best yields at both temperatures are with the use of concentrated acid showing that the hydrochloride formed by strong acid was more soluble at these temperatures than at 20°. The best yield was with concentrated HCl acid at 60° giving 75.4% of the theoretical and 91% correcting for solubility of the chromate salt.

Curve IV gives the per cent yields at 100° with different concentrations of acids. The best yield being with 10% HCl; although all the yields seem to indicate that with the high temperatures the hydrazoanisol was oxidized slightly to the azo

compound. This was especially true of the conversion using concentrated acid and high temperatures.

As the temperature increases in each case the solutions became more highly colored, generally a dark blue.

The rearranged hydrazoanisol was first precipitated in the form of the sulfate, but the yields obtained were only 50% of the theoretical. For this reason the dinisidine was precipitated in the form of the chromate and 74.5% of the theoretical yield was obtained, and 91% with the solubility correction.

The solubility corrections for the chromate salt are given by Curve V for the different concentrations of acid at 20°.

40%

30%

20%

10%

0% 10 20 30 40 50 60 70 80 90 100%

6

CURVE I. at 20

Comparison of Rearrangement
after 30 minutes

1. 2% HCl	69.5% yields
2. 3% HCl	60.0% "
3. 5% HCl	51.7% "
4. 7.5% HCl	36.6% "
5. 10% HCl	35.6% "
6. 37% HCl	28.4% "
	"

40%

30%

20%

10%

0% 10 20 30 40 50 60 70 80 90 100%

6

CURVE II at 40

Comparison of rearrangement
after 30 minutes

1. 2% HCl	42.4% yields
2. 3% HCl	46.5% "
3. 5% HCl	51.4% "
4. 7.5% HCl	52.8% "
5. 10% HCl	58.3% "
6. 37% HCl	62.9% "

Curves without solubility corrections

— 1970
— 1971
— 1972

40%

CURVE III. at 60
Comparison of Rearrangement
after 30 minutes time

30%

20%

10%

0

10

20

30

40

50

60

70

80

90

100%

0

60

10

20

30

40

50

60

70

80

90

100

110

120

130

140

150

160

170

180

190

200

210

220

230

240

250

260

270

280

290

300

310

320

330

340

350

360

370

380

390

400

410

420

430

440

450

460

470

480

490

500

510

520

530

540

550

560

570

580

590

600

610

620

630

640

650

660

670

680

690

700

710

720

730

740

750

760

770

780

790

800

810

820

830

840

850

860

870

880

890

900

910

920

930

940

950

960

970

980

990

1000

1. 2	% HCl	41.1	Yield
2. 3	% HCl	44.5	"
3. 5	% HCl	48.2	"
4. 7.5	% HCl	54.6	"
5. 10	% HCl	67.9	"
6. 37	% HCl	75.4	"

CURVE IV. at 100

Comparison of Rearrangement
after 30 minutes time

40%

30%

20%

10%

0

10

20

30

40

50

60

70

80

90

100

110

120

130

140

150

160

170

180

190

200

210

220

230

240

250

260

270

280

290

300

310

320

330

340

350

360

370

380

390

400

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430

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470

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490

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530

540

550

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650

660

670

680

690

700

710

720

730

740

750

760

770

780

790

800

810

820

830

840

850

860

870

880

890

900

910

920

930

940

950

960

970

980

990

1000

60

1. 2 % HCl

38.9 % Yield

2. 3 % HCl

41.7 % "

3. 5 % HCl

45.2 % "

4. 7.5 % HCl

51.7 % "

5. 10 % HCl

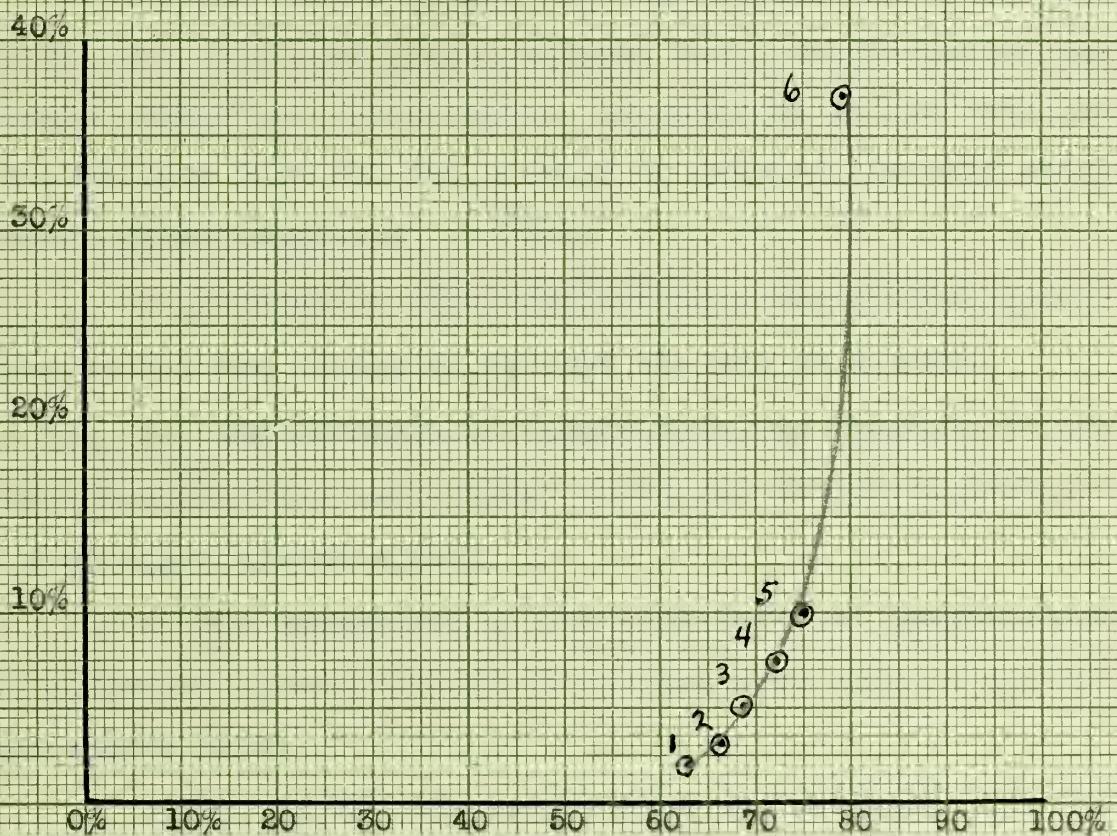
61.2 % "

6. 37 % HCl

55.0 % "

Curves without solubility corrections

CURVE V. at 20°
Yields of pure Dinitroidine Chromate
showing losses due to solubility



			yield
1.	1% HCl	63.2 %	"
2.	3% HCl	66.6 %	"
3.	5% HCl	68.6 %	"
4.	7.5% HCl	72.2 %	"
5.	10% HCl	75.3 %	"
6.	37% HCl	79.9 %	"

1000000
100000
10000

SUMMARY.

1. Large quantities of alcohol are not needed to prepare hydrazoanisol from O-nitroanisol, for by the use of the "sieve method" good yields are obtained and water is substituted to a large extent for alcohol.

2. The "sieve method" for the separation of hydrazoanisol from the zinc and zinc oxide residues was found to be the most efficient method of preparation. In addition to its simplicity it allows less time for the product to oxidize, thereby obtaining a purer hydrazo compound.

3. No results were obtained when the preparation of hydrazoanisol was attempted without the use of alcohol.

4. The chromate of dianisidine was found to be less soluble than ^{the} sulfate and better suited for the precipitation of the rearranged hydrazoanisol.

5. The comparison of the conversion of hydrazoanisol with different concentrations of hydrochloric acid at different temperatures show:

First, at 20° the best yields are obtained with 2%-7.5% acid.

Second, at 40° and 60° the best yields are obtained with concentrated acid.

Third, at 100° the yields are lower due to partial oxidation of the hydrazoanisol.

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